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Kinetic Studies of UV/Vis-Chemiluminescence in the CH + O$_2$ Gas Phase Reaction

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Abstract

CO uv/vis-chemiluminescence has been observed for the first time in the 248-nm photodissociation of a trace amount of bromoform (CHBr$_3$) vapor present in an excess of O$_2$ and in diluent helium carrier gas at 2 torr and at 298 K. The integrated intensities of the time-resolved chemiluminescence traces due to characteristic CO(A-X), CO(a-X) and CO(d-a) vibronic emissions showed quadratic dependence on the 248-nm photolysis laser fluence used. The decay kinetics of these chemiluminescences was studied as a function of added [H$_2$], [D$_2$], [N$_2$], [CH$_4$], [O$_2$] and [CHBr$_3$], and comparisons made to the behavior of the concurrently recorded OH(A-X)-chemiluminescence in the system. The CH(X$^2\Pi$) + O$_2$ reaction has previously been identified as the main source for the OH(A-X) emissions in such photolyses. Here, we show that the CH(a$^4\Sigma^-$) + O$_2$ reaction can also be a minor source for the OH(A-X) emission, and that this reaction may also be partly responsible for the observed CO emissions. Besides from the methylidyne (CH(X$^2\Pi$) and CH(a$^4\Sigma^-$)) radicals, the bromomethyne (CBr) and the dibromomethylene (CBr$_2$) radicals can also be produced in the 2-photon photolysis of CHBr$_3$, and their reactions with O$_2$ may explain the source for the bulk of the observed CO-chemiluminescence. Future comparisons of CBr$_4$, CBr$_3$F and CBr$_2$F$_2$ photolyses in the presence of O$_2$ and/or O-atoms may provide some insight as to which of the radical species is the dominant precursor for the CO-chemiluminescence observed here.

Introduction

The methylidyne (CH) radical is known to be an important reaction intermediate during the oxidation of hydrocarbon fuels. Its reactivity with combustion species such as O$_2$, O-atoms, CO$_2$, N$_2$, N$_2$O, NO, NO$_2$, NH$_3$ and numerous other hydrogenous, carbonaceous and sulfurous species is well reviewed[1,2] and compiled in the literature.[3] However, the nature of product branching, energy disposal and its theoretical treatment has been examined in only a few of these reactions; (CH + NO) and (CH + N$_2$) reactions by far being the most studied systems. Particularly lacking in the literature is information on the production of electronically excited state species. The methylidyne and the methylene (CH$_2$) radical reactions with O$_2$ and O-atoms are thought to play an important role in the production of ultraviolet/visible chemiluminescence when the Space Shuttle plume interacts with the earth's ambient atmosphere.[4] Our results on the (CH + O-atoms), (CH$_2$ + O-atoms) and (CH$_2$ + O$_2$) reaction systems will be the subject of detailed discussions in future publications.

For the O$_2$ reaction with ground state CH, a number of exothermic channels (with ground state products) are possible:

$$\Delta H^o_{298K} (\text{kcal mol}^{-1})$$

$$CH(X^2\Pi) + O_2(X^3\Sigma_g^-) \rightarrow CO(X^1\Sigma^+) + OH(X^2\Pi) \qquad (-159.1) \ (1)$$
$$\rightarrow CO_2(X^1\Sigma_g^+) + H(^2S) \qquad (-184.0) \ (2)$$
$$\rightarrow HCO(X^2A') + O(^3P) \qquad (-72.4) \ (3)$$
$$\rightarrow H(^2S) + CO(X^1\Sigma^+) + O(^3P) \qquad (-56.7) \ (4)$$
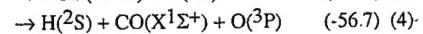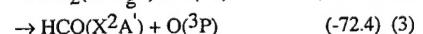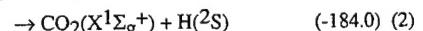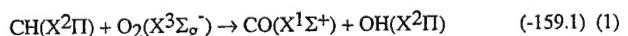
The overall bimolecular room temperature rate coefficient value lies in the range (2.3-5.9) x 10^{-11} cm^3 molec^{-1} s^{-1} amid the various reported works and shows no pressure dependence in 2-350 torr of Ar or He.[5-18] Okada and co-workers[13] have reported a small OH(X$^2\Pi$) product yield of ~ 0.20 at 297 K. During the tenure of this work, we became aware of Bergeat and co-workers[18] estimates for the branching ratios of 20%, 30%, 20%, and 30% for channels (1), (2), (3), and (4), respectively. Previously, Lin[8] had observed strong CO$_2$ and CO ir-emissions, as a result of vibrational excitation, presumably through their direct formation in channels (2) and (1), respectively.


The availability of 159.1 kcal mol^{-1} of enthalpy in channel (1) can provide a means of exciting one of the reaction products into a higher electronic state. Previously,[5,7,8,14,18,19,20] uv-chemiluminescence attributable to the formation of electronically excited hydroxyl (OH) radicals has been reported in this reaction:

$$CH(X^2\Pi) + O_2(X^3\Sigma_g^-) \rightarrow CO(X^1\Sigma^+) + OH(A^2\Sigma^+) \qquad (-66.6) \quad (1b)$$
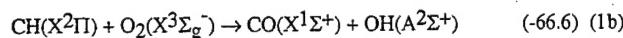
The reaction is thought, in part, to be responsible for the strong characteristic OH(A→X) emissions in hydrocarbon flames.[20] Grebe and Homann,[14] and Porter et al.[19] have provided estimates for the 298 K yield of OH(A$^2\Sigma^+$) to be ~ 0.0048 and ~ 0.0060, respectively. Electronically excited carbon monoxide may form in channel (1c):

$$CH(X^2\Pi) + O_2(X^3\Sigma_g^-) \rightarrow CO(a^3\Pi, a'^3\Sigma^+) + OH(X^2\Pi) \quad (20.5, -0.8) \quad (1c)$$
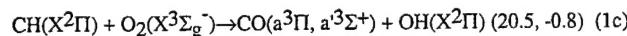
Higher electronic states of CO such as (d$^3\Delta$) and (A$^1\Pi$) might also be possible if the methylidyne radical used is vibrationally excited. These CO states should experimentally be readily observable through their ultraviolet emissions in the (a$^3\Pi \rightarrow X^1\Sigma^+$) Cameron system, ir/visible emissions in the (a'$^3\Sigma^+ \rightarrow a^3\Pi$) Asundi and (d$^3\Delta \rightarrow a^3\Pi$) Triplet systems, and vuv emissions in the (A$^1\Pi \rightarrow X^1\Sigma^+$) 4th Positive system.

In this paper we present first ever measurements of the time-resolved CO uv/vis-emission profiles observed when CHBr$_3$ vapor is photodissociated at 248 nm in the presence of O$_2$ in He bath gas at 2.0 torr and at 298 K. The observations are discussed in terms of the O$_2$ reaction with the CH photoproduct as the likely source for the CO-chemiluminescence. Alternate O$_2$ reactions with other possible photoproducts such as CBr and CBr$_2$ will also be discussed.

Experimental Technique

The pulsed-photolysis apparatus used in this work has previously been described in detail elsewhere.[21,22] Here we only give the experimental procedures used to record the chemiluminescence data. A minute amount of bromoform (CHBr$_3$) vapor entrained in a small flow of He was sent into an ultraviolet photometric cell to determine its gas phase concentration before diluting it further in a larger flow of He carrier gas containing a known excess of O$_2$. An uv-absorption cross-section, $\sigma_{213.9-nm}$, of 524 x 10^{-20} cm^2 molec[-1] for the CHBr$_3$ was used.[23] Previously calibrated electronic mass flow transducers, chromel-alumel thermocouples and capacitance manometers were used to introduce the gases into the photolysis reactor and monitor the system's temperature (typically (298 ± 2) K) and pressure

(typically (2.0 ± 0.1) torr). A collimated 248-nm beam from a pulsed excimer laser (width ~ 20 ns, full-width at half-maximum, FWHM) operating at 10 Hz was gently focused into the photolysis reactor and its fluence determined at a disc colorimeter positioned at the exit window of the reactor. Typically (1-10) x 10[12] molec cm^{-3} of CHBr$_3$ was subjected to 5-40 mJ/pulse of laser energy to produce transient levels of CH concentrations via multi-photon dissociation of the bromoform.[24-28] The photolysis reactor was operated under quasi-static gas flow conditions. That is, the He flow was sufficiently rapid to ensure that the reaction zone was replenished with a fresh mixture of the photolyte upon each laser pulse, but was slow enough to be considered static when compared to the time scale of the chemical reaction of the CH radicals with the O$_2$ ((7-100) x 10[13] molec cm^{-3}), plus with the undissociated CHBr$_3$, and also to a lesser extent with any other species produced in the photolysis. The uv/vis-chemiluminescence that ensued from the detection zone was monitored perpendicular to the photolyzing beam by imaging the radiation onto the entrance slits of two different scanning spectrometers positioned opposite to each other. The operating ranges of the spectrometers were 110-360 nm and 200-900 nm, and had, respectively, band-passes set to 1.9 and 2.2 nm, FWHM. Appropriate long-pass glass filters were placed in front of the spectrometer when recording visible emissions to block the strong uv-radiation from entering the instrument and thus prevent any coincidental detection of its higher-order diffracted signal. The photomultipliers used to detect the radiation were configured for single-photon counting detection, the outputs of which were sent for recording at two separate multi-channel scalers controlled by a microcomputer. Time-resolved temporal profiles of the chemiluminescence, at several discrete CO and OH vibronic band positions, were recorded using a 10-μs dwell-time resolution. 50000 chemiluminescent traces were typically co-added at the computer to improve the signal-to-noise ratio of each of the data sets. The behavior of these decays was studied as a function of the added substrate (H$_2$, D$_2$, N$_2$, CHBr$_3$ and CH$_4$) concentrations.

Results and Discussion

Production of CH from CHBr$_3$ photolysis is well known, and at 248 nm 2-photon absorption must take place to produce the radical.[24-28] Since the initial methylidyne radical concentration, [CH]$_0$ is expected to be very low compared to the initial photolyte concentration, [CHBr$_3$]$_0$ or the [O$_2$] employed the methylidyne is expected to react away under pseudo-first-order conditions with these species as the contribution from its self-reaction will be negligible in our photolysis. It can be shown that:

$[OH(A,v'=1)] =$
$k_{1b(v'=1)}[CH]_0[O_2]\{exp(-k_{CH} \cdot t)\ exp(k_{OH(A,v'=1)} \cdot t)\}/(k_{OH(A,v'=1)}$-$k_{CH})$ (5)

Where $k_{CH} = k_{O_2}[O_2] + k_{CHBr_3}[CHBr_3] + k_{loss}$ is the pseudo-first-order rate coefficient for [CH] decay in the system, with k_{O_2} and k_{CHBr_3} as the second-order bimolecular rate coefficients for reaction of ground state CH with O_2 and $CHBr_3$, respectively. k_{loss} is the sum of first-order loss rate terms for diffusion of CH out of the reaction volume and for reaction with any background species that may be present in the photolysis mixture. $k_{1b(v'=1)}$ is the specific branching rate coefficient for the channel that gives $OH(A,v'=1)$ as the product in the (CH + O_2) reaction. $k_{OH(A,v'=1)} = k_{rad(v'=1)} + k_{q,O_2}[O_2] + k_{q,CHBr_3}[CHBr_3] + k_{OH(A,v'=1)loss}$ is the pseudo-first-order rate coefficient for $[OH(A,v'=1)]$ decay in the system, with k_{q,O_2} and $k_{q,CHBr_3}$ as the second-order bimolecular rate coefficients for quenching (vibrational and electronic) of $[OH(A,v'=1)]$ by O_2 and $CHBr_3$, respectively. $k_{rad(v'=1)}$ and $k_{OH(A,v'=1)loss}$ are, respectively, the $[OH(A,v'=1)]$ first-order rate coefficients for radiative decay to the ground electronic state and the sum of loss rate terms for diffusion of $OH(A,v'=1)$ out of the detection volume and for reaction with any background impurities.

Since the value of $k_{OH(A,v'=1)}$ is very large and our shortest time resolution is 10 µs, experimentally we expect to see an instantaneous rise in the 282-nm OH signal followed by its single-exponential decay. The integrated I_{282} intensity over this decay time will be directly proportional to the initial yield of $[CH]_0$ in the photolysis, and therefore to the square of the laser fluence, $(E_{248})^2$ provided there are no saturation absorption effects in the range of the laser fluences employed. Figure 1, shows a typical OH(1-0)-chemiluminescence curve observed. The ln[integrated I_{282} intensity] of such curves is plotted as a function of ln[E_{248}] in Figure 2. A linear-least-square fit to the data points yields a value of (1.96 ± 0.22) for the slope thus confirming the 2-photon production of CH in the photolysis. The chemiluminescence intensity and its decay rate were dependent on the $[O_2]$, and as Figure 1 shows the decay exhibited a non-exponential behavior. We attribute this to more than one distinct radical species reacting with the O_2 to produce the OH(A). The OH(A-X)-chemiluminescence would then be given by a sum of the RHS expressions of Equation (5) for each independent contributing species.
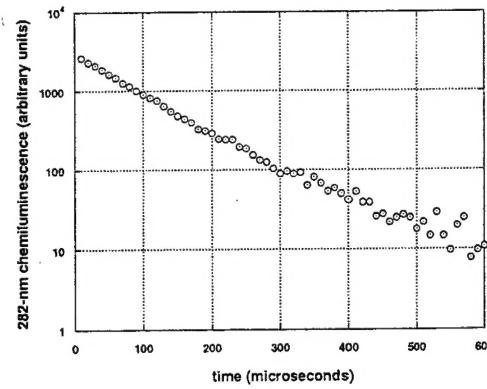

Fig. 1 Typical 282-nm $OH(A^2\Sigma^+,v'=1 \rightarrow X^2\Pi,v''=0)$ time-resolved chemiluminescence trace observed immediately after the 248-nm photolysis of a $CHBr_3/O_2$ mixture at 298 K in 2.0 torr of He.
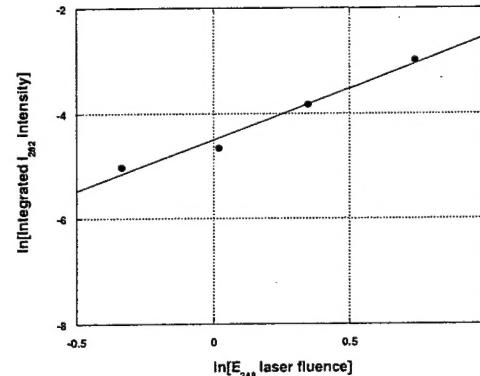

Fig. 2 A plot of ln[Integrated I_{282} intensity] as a function of ln[E_{248} laser fluence].

By studying the behavior of the OH chemiluminesence decay kinetics in the presence of added methane, it was shown that there was a rapid and proportional decay of the chemiluminesence at early reaction times with the $[CH_4]$ employed, but at longer times the decay rate remained essentially unaffected. This behavior is consistent with the rapid removal of the $CH(X^2\Pi)$ precursor and slow removal of the $CH(a^4\Sigma^-)$ precursor by the CH_4, with our measured rate coefficient values of 5.7 x 10^{-11} and < 3 x 10^{-13} cm^3 molec^{-1} s^{-1}, respectively. Experiments were carried out with an excess of CH_4 such that the $CH(X^2\Pi)$ was removed from the system within 10-20 µs. The decay kinetics of the weak but persistent OH-chemiluminesence was then studied as a function of

3

added [O$_2$] to obtain the CH(a$^4\Sigma^-$) + O$_2$ rate coefficient value of 2.2 x 10^{-11} cm^3 molec^{-1} s^{-1}. Under these conditions adding H$_2$, D$_2$ or N$_2$ had a negligible effect on the decay rate, consistent with the fact that CH(a$^4\Sigma^-$) is known not to react with these species.[29] Also, the integrated intensity of this persistent OH-chemiluminescence showed a quadratic laser fluence dependence. When no CH$_4$ was present in the system, the early time OH-chemiluminesence decay kinetics was investigated as a function of [O$_2$], [H$_2$], [D$_2$], [N$_2$] and [CHBr$_3$]. The respective rate coefficients obtained are, 3.6 x 10^{-11}, 1.4 x 10^{-12} (in 2-torr He), 5.5 x 10^{-11}, 2 x 10^{-13} (in 2-torr He), and 6.0 x 10^{-10} cm^3 molec^{-1} s^{-1}. These values are consistent with the known reactivity of the CH(X$^2\Pi$) with these reagents.[29] CH(X$^2\Pi$) is therefore the principal OH(A) producing precursor in our photolysis system. The overall 1-σ uncertainty in the rate coefficient values is ~ ± 18%, precision plus systematic.

Since the O$_2$ is not expected to dissociate at 248 nm to produce O-atoms, one can obtain an expression similar to that of Equation (5) for [CO(A)] during CHBr$_3$/O$_2$ photolysis. Figure 3 shows typical CO(A-X)-chemiluminescence decays observed. The integrated I$_{165.3}$ intensity showed a (1.92 ± 0.09) laser fluence dependence. Similar 2-photon dependencies were also confirmed for the 215.7-nm-CO(a-X) and 643.6-nm-CO(d-a) emissions. The 165.3 nm curves again exhibited non-exponential behavior suggesting multiple photo-precursor species reacting with the O$_2$. However, as before, it was possible to fit the data to a single exponential at early reaction times to evaluate the O$_2$ reaction rate coefficient for the most reactive CO(A-X) precursor.
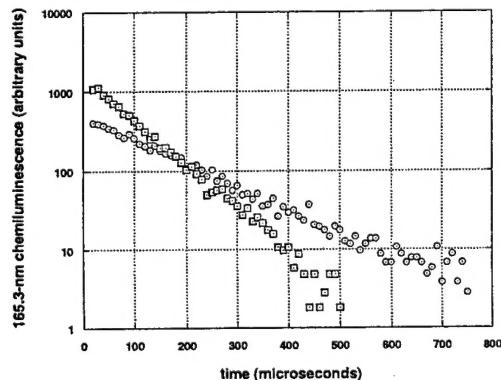
mixtures at 298 K in 2.0 torr of He. The [CHBr$_3$] was 1.5 x 10^{12} molec cm^{-3}, and [O$_2$] was 8.03 x 10^{13} (circles) and 17.2 x 10^{13} molec cm^{-3} (squares).

Figure 4 shows the second-order plots obtained when such analysis was performed when the 165.3-nm-CO and 282-nm-OH-chemiluminescence traces are recorded at the two spectrometers. The O$_2$ reaction rate coefficient of 6.3 x 10^{-11} cm^3 molec^{-1} s^{-1} evaluated from 165.3-nm-CO traces is much larger than that determined from the 282-nm-OH traces (3.6 x 10^{-11} cm^3 molec^{-1} s^{-1}). This suggests either a different precursor, X, for CO(A-X) production in our system, or that the vibrationally excited methylidyne radical, CH(X$^2\Pi$, v'≥4) that is necessary for generating the observed CO-4th Positive emissions has a much higher reactivity with the O$_2$ than the ground state (GS) species, CH(X$^2\Pi$, v''=0) which is known to give OH(A).[14,19] Because the initial GS concentration, [CH(X$^2\Pi$, v''=0)]$_0$ is expected to be much larger than the concentrations, [CH(X$^2\Pi$, v''≥0)]$_0$, of any of the initially produced vibrationally excited state species, any contributions to OH(A) production from such species should be small. Our rate coefficient value for the methylidyne radical + O$_2$ interaction determined from OH(A-X) traces is indeed, within experimental errors, identical to that expected for the true value for CH + O$_2$ GS-reaction determined by direct LIF monitoring of the CH(X$^2\Pi$, v''=0).[5,6,10,13,15,16,17,18,24]
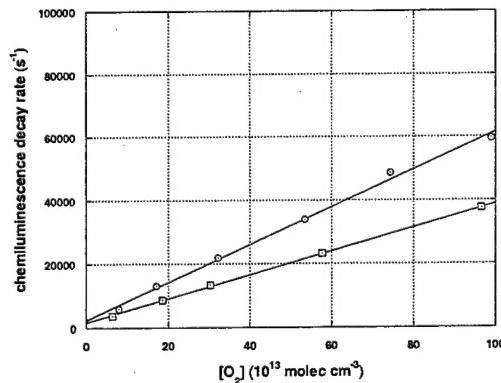
Fig. 4   Second-order plots of 165.3-nm-CO chemiluminescence (open circles) and 282-nm-OH chemiluminescence (open squares) decay rates as a function of [O$_2$] at 298 K and in 2.0 torr of He.

To our knowledge there is no kinetic data available in the literature on the reactivity of CH(X$^2\Pi$, v''=4) radical. However, for 1 vibrational quanta in the CH(X$^2\Pi$)

Fig 3. Typical 165.3-nm CO(A$^1\Pi$,v'=0 → X$^1\Sigma^+$,v''=2) time-resolved chemiluminescence traces observed immediately after the 248-nm photolysis of CHBr$_3$/O$_2$

radical, previous kinetic studies[13,16] have shown that its reactivity towards O_2 is essentially the same as that of the GS species. Further more, it is known that H_2, D_2 and N_2 have large and pressure independent rate coefficients with $CH(X^2\Pi, v''=1)$. Here we investigated the behavior of the CO(A-X)-chemiluminescence decay in the presence of these three substrates, to see if we could identify our species X with the $CH(X^2\Pi, v''=4)$ radical. One would anticipate that the $CH(X^2\Pi, v''=4)$ radical might have similarly high reactivity towards these species. Both H_2, and D_2 efficiently suppressed only the faster 165.3-nm chemiluminescence component from the system, while the slow decaying portion of the chemiluminescent signal essentially remained unchanged. Similar observations were seen when CH_4 was added and when $[CHBr_3]$ was varied. However, addition of N_2 had no major effect on any part of the CO-chemiluminescent trace. We measured the reaction rate coefficients to be; 6.4×10^{-11}, 3.3×10^{-11}, 1.9×10^{-10}, 9.0×10^{-10} and 8×10^{-13} cm^3 molec^{-1} s^{-1}, respectively for these added species. The above observed large rate coefficients would be consistent with X as being $CH(X^2\Pi, v''=4)$, and that for reasons not yet clear to us the N_2 has a reduced reactivity, while the O_2 an enhanced reactivity for the methylidyne radical in this vibrational state. Alternatively, it could well be that the N_2 and O_2 results are suggesting that the species X is an entirely different species such as the bromomethyne (CBr) or the dibromomethylene (CBr_2) radical. Since their GS reactions with O_2 would not be energetic enough to produce CO(A), they would need to be produced internally excited in the 2-photon dissociation of the $CHBr_3$. However, recent work[30] on $CHBr_3$ photolysis indicates that the dibromomethylene does not form. Therefore we prefer our alternate choice for X to be the bromomethyne, (CBr, v'') radical. Again it is to be noted that the GS bromomethyne radical reacts slowly with the O_2 with a reported room temperature rate coefficient of 1.5×10^{-12} cm^3 molec^{-1} s^{-1}.[31]

The persistence of the CO-chemiluminescence even in a large excess of $[CH_4] = 5 \times 10^{15}$ molec cm^{-3} suggests the presence of another precursor, X' that reacts slowly with the O_2. The decay kinetics of X' was investigated by adding H_2, D_2, N_2 and O_2 to the system under these conditions. Here, H_2, D_2 and N_2 did not substantially affect the decay rate of the CO-chemiluminescence, and their respective reaction rate coefficients for the removal of X' were determined to be 2×10^{-14} and 9×10^{-14} and 6×10^{-13} cm^3 molec^{-1} s^{-1}. The X' + O_2 reaction rate coefficient was determined to be 1.9×10^{-11} cm^3 molec^{-1} s^{-1}. Also, the CO(A-X) emission that arose due to the X'

precursor showed a quadratic laser fluence dependence. Since the CO(A-X) emission cannot be efficiently quenched by the amount of methane employed, a direct comparison of the chemiluminescence signal strengths was made in the absence and in the presence of excess CH_4. The X' + O_2 reaction represents only ~ 5% of the total CO-chemiluminescence source strengths. Since the relative yields of $[X]_0$ and $[X']_0$ are not known, no information can be ascertained above the relative branching efficiencies for producing CO(A) in these two reactions.

Since the CO(A-X)-chemiluminescence decay kinetics due to H_2, D_2, N_2 and O_2 in excess methane very closely resembled to that of the OH(A-X)-chemiluminescence decay kinetics with these species also under such methane conditions, we propose the identity of X' to be $CH(a^4\Sigma^-)$. However, it must be noted that for $CH(a^4\Sigma^-)$ + O_2 reaction to produce the observed CO-4th Positive emissions, the quartet methylidyne radical must possess additional internal energy equivalent to at least 2 quanta of vibrations. This also suggests that the GS quartet and the $CH(a^4\Sigma^-, v''=2)$ species react at the same rate with the O_2, and that CH_4, H_2, D_2 and N_2 are inefficient at vibrationally relaxing $CH(a^4\Sigma^-, v''=2)$.

Conclusions

Our kinetics studies have identified for the first time that OH(A) can be produced in the $CH(a^4\Sigma^-)$ + O_2 reaction. The measured overall rate coefficient for this reaction is consistent with that derived in chemi-ion kinetics studies of Hou and Bayes.[29] This reaction can also produce electronically excited CO products, and is partially responsible for the CO(A-X) emissions we have observed during the 248-nm photolysis of $CHBr_3/O_2$ mixtures. The source for the bulk of the CO-chemiluminescence observed in these experiments is most likely to be the O_2 interaction with $CH(X^2\Pi, v''\geq4)$ radicals or with highly vibrationally excited (CBr, v'') radicals. The production of these radicals from $CHBr_3$ requires the absorption of at least two quanta of radiation during the photolysis. Our observed quadratic dependencies of the integrated OH-chemiluminescence and CO-chemiluminescence signals on the photolysis laser fluence employed is consistent with this dissociation mechanism for $CHBr_3$. Future comparisons of chemiluminescence studies in CBr_4, CBr_3F and CBr_2F_2 photolyses in the presence of O_2 and/or O-atoms may provide some insight as to which of the radical species is the dominant precursor for the CO-chemiluminescence observed here.

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